## SUPPORTING INFORMATION n ${ }^{\circ} 1$




(Computed)

Anti
(Computed)

Experimental
(X-ray)

Top: MMX computed structures of the anti and syn conformational diastereoisomers of $\mathbf{1}$. Bottom: single diastereoisomer observed by X-ray diffraction.

## SUPPORTING INFORMATION n ${ }^{\circ} 2$



Left: experimental ${ }^{1} \mathrm{H}$ NMR ( 300 MHz ) signals of the hydrogen in position 3 of the phenyl ring of compound $\mathbf{2}$ in toluene-d8 as function of temperature. Right: computer simulation obtained with the rate constants reported.

## SUPPORTING INFORMATION n ${ }^{\circ} 3$

## Synthesis of 1,2-bis(1-naphthyl)-4-nitrobenzene (3) from 3,4-dinitrothiophene

Compound 3 was prepared through a proper adaptation of a reported procedure* starting from 1,4-bis(diethylamino)-2,3-dinitro-1,3-butadiene, easily obtainable via a ring-opening reaction of 3,4dinitrothiophene with diethylamine. \#

1,2-Bis(1-naphthyl)-4-nitrobenzene (3). A solution of ( $E, E, E$ )-1,6-bis(1-naphthyl)-3-nitro-1,3,5hexatriene ( 0.4 mmol ), iodine ( 2 mmol ) and cyclohexene oxide ( 0.8 mmol ) in toluene $(500 \mathrm{~mL})$ was heated overnight at $80^{\circ} \mathrm{C}$. Usual workup* and purification by column chromatography gave 0.37 mmol (92\%) of $\mathbf{3}$ with physical and spectroscopic data in agreement with those reported in the Experimental Section.
( $E, E, E)$-1,6-Bis(1-naphthyl)-3-nitro-1,3,5-hexatriene.
1,4-Bis(diethylamino)-2,3-dinitro-1,3butadiene ( 1 mmol ) in THF ( 30 mL ) was reacted, under argon and at $0{ }^{\circ} \mathrm{C}$, with (1naphthyl)methylmagnesium bromide ( 4 mmol ) freshly prepared in THF/xylene ( $5: 1 \mathrm{l}, \mathrm{v} / \mathrm{v}$ ). After 30 min , the reaction mixture was poured into a dichloromethane $/ \mathrm{ice} / \mathrm{HCl}(4 \mathrm{mmol})$ mixture and worked up as reported.* The title hexatriene was obtained in $81 \%$ yield as a red solid, m.p. $104.7-105.3^{\circ} \mathrm{C}$ (dichloromethane-light petroleum); ${ }^{1} \mathrm{H}-\mathrm{NMR}\left(\mathrm{CDCl}_{3}, 200 \mathrm{MHz}\right) \delta 7.20$ and $7.29(\mathrm{~d}, J=16.2 \mathrm{~Hz}, 2 \mathrm{H}$ in total), $7.53(\mathrm{~m}, 7 \mathrm{H}), 7.87$ and 8.11 (two m partly overlapped, 10 H in total); ${ }^{13} \mathrm{C}-\mathrm{NMR}\left(\mathrm{CDCl}_{3}, 50\right.$ $\mathrm{MHz}) \delta 119.14,123.07,123.45,124.39,124.46,124.86,125.62,125.74,126.26,126.44,126.80$, $127.14,128.90,129.02,129.63,130.61,131.29,132.89,133.66,133.80,133.91,134.15,135.02$, 137.88, 141.52, 148.03. Anal. Calcd for $\mathrm{C}_{26} \mathrm{H}_{19} \mathrm{NO}_{2}$ : C, 82.74 ; H, 5.07; N, 3.71. Found: C, 82.83; H, 5.15; N, 3.66.

* Dell'Erba, C; Gabellini, A.; Mugnoli, A.; Novi, M.; Petrillo, G.; Tavani, C. Tetrahedron 2001, 9025.
\# Dell'Erba, C.; Mele, A.; Novi, M.; Petrillo, G.; Stagnaro, P. Tetrahedron Lett. 1990, 31, 4933. Dell'Erba, C.; Mele, A.; Novi, M.; Petrillo, G.; Stagnaro, P. Tetrahedron 1992, 48, 4407.

